# Communication—Lithium Ion Concentration Effect in PYR$_{14}$TFSI Ionic Liquid for Li-O$_2$ Battery Cathodes

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The oxygen reduction reaction (ORR) has been studied on Au cathodes in O$_2$ saturated PYR$_{14}$TFSI ionic liquid (IL) electrolyte using cyclic voltammetry, rotating ring disc electrode (RRDE), electrochemical quartz crystal microbalance (EQCM) and differential electrochemical mass spectrometry (DEMS). At different Li$^+$ concentrations in the IL competition of Li$^+$ and PYR$_{14}^+$ for superoxide ion results in dismutation of Li$^+$O$_2^-$ and formation of insoluble Li$_2$O$_2$.

Ionic liquids (ILs) are promising electrolytes for metal-air batteries since they are non volatile, non flammable and liquid at room temperature with high oxygen solubility, and high stability particularly for Li-O$_2$[1,2] and Na-O$_2$[3–5] batteries. One of the most widely investigated ILs for metal-O$_2$ batteries is N-butyl-N-methylpyrrolidinium bis(trifluoro-methane sulfonyl)amide (PYR$_{14}^+$ TFSI$^-$ also denominated [C4mpyr][TFSI].[6]

In ionic liquids, including PYR$_{14}$TFSI, in the absence of protons and alkali metal ions, the reversible formation of O$_2$/O$_2^-$ couple is observed[6–12] due to the stabilization of superoxide radical ion by IL cation like the tetralkyl ammonium cations in aprotic organic solvents. However, the ORR in ionic liquids changes in the presence of alkali metal ions, especially in the presence of the small Lewis acid Li$^+$ cation.[13,14] Allen et al.[15,16] described the mechanism of ORR in PYR$_{14}$TFSI in 25 mM Li$^+$ as follows:

$$Li^+ + O_2 + e \rightarrow LiO_2 \qquad [1]$$

$$2LiO_2 \rightarrow Li_2O_2 + O_2 \qquad [2]$$

$$PYR_{14}^+ + O_2 + e \rightarrow PYR_{14}^+ - O_2^-. \qquad [3]$$
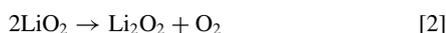
Following for the oxygen evolution reaction (OER) in the anodic sweep:

$$PYR_{14}^+ - O_2^- \rightarrow PYR_{14}^+ + O_2 + e \qquad [4]$$

$$LiO_2 \rightarrow Li^+ + O_2 + e \qquad [5]$$

$$Li_2O_2 \rightarrow 2Li^+ + O_2 + 2e \qquad [6]$$
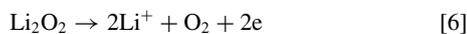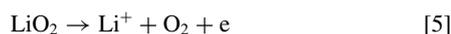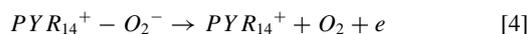
Herranz et al. have quantified the stability of pure PYR$_{14}$TFSI in the presence of superoxide with RRDE.[17] The stability of PYR$_{14}^+$ studied by FTIR has been reported recently.[18]

Briefly, in oxygen saturated LiTFSI containing PYR$_{14}$TFSI electrolyte carbon dioxide and water were formed at potential 4.3 V either with or without previous O$_2$ electroreduction reaction. However in deoxygenated LiTFSI contacting ionic liquid no formation of CO$_2$ or water was observed, suggesting oxygen presence to be crucial in carbon dioxide production.

In this communication we report for the first time RRDE ORR experiments in PYR$_{14}$TFSI ionic liquid containing Li$^+$ at concentrations from 0 to 50 mM, complemented by EQCM and DEMS, and discuss the mechanism of ORR in this ionic liquid.

## Experimental

Anhydrous N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl) amide PYR$_{14}$ TFSI, (Io-Li-Tec) and bis(trifluoromethane) sulfonimide lithium salt (544094, LiTFSI, sigma Aldrich) were stored in the argon-filled MBRAUN glove box with an oxygen content $\leq$ 0.1 ppm and water content below 2 ppm. All solutions were prepared inside the glove box, dried for several hours at 80°C under vacuum and the water content was measured using the Karl Fisher 831 KF Coulometer (Metrohm). Solutions were found to contain around 20 ppm of water.

Rotating ring disc electrode (RRDE) system has been described in details elsewhere. An Au/Au RRDE with r$_1$ = 0.25, r$_2$ = 0.26, and r$_3$ = 0.30, where r$_1$ is the radius of disc electrode, r$_2$ and r$_3$ are respectively the inner and outer radii of the RRDE system with a geometric area of 0.196 cm$^2$, and collection coefficient 0.28 was employed.

The reference Li$_2$Mn$_2$O$_4$/LiMn$_2$O$_4$ electrode (2.61 V Li/Li$^+$ in PYR$_{14}$TFSI) was used and potentials herein are quoted with respect to the Li/Li$^+$ scale in 0.1 M Li$^+$ in PYR$_{14}$TFSI.[18] Electrode potential calibration with ferrocene was done.

A large area Pt gauze was the counter electrode. The Pt counter electrode was not shielded during the electrochemical measurements, however it was positioned far enough from the working electrode in order to avoid possible contamination of the electrolyte with its oxidation by-products, moreover the ionic liquid is viscous and the diffusion of side products is expected to be slow.

Differential electrochemical mass spectrometry (DEMS) was accomplished using a Pfeiffer vacuum Omnistar GSD 320 gas analysis system with a quadrupole mass spectrometer QGM 220 (mass range 1−200 amu) with ion gastight ion source, yttriated iridium-filament with secondary electron multiplier C-SEM and Faraday detectors. The DEMS cell setup was used as described elsewhere.[18] An EQCM system with shear wave dissipation that has been described elsewhere[19] has been employed.

For the experiments the Li$^+$ was added stepwise in order to increase the Li$^+$ concentration in the ionic liquid, however the RRDE was dissembled prior each measurement an its surface was cleaned and polished with 0.05 μm alumina. The procedure was done in order to clean any possible ORR products side products, such as passivating Li$_2$O$_2$ or Li$_2$CO$_3$ films.

## Results and Discussion

Figure 1 depicts cyclic voltammetry of an Au electrode in PYR$_{14}$TFSI + LiTFSI at different Li$^+$ concentrations, 0–50 mM, at 50 mV.s$^{-1}$. In pure ionic liquid PYR$_{14}$TFSI a quasi-reversible one-electron wave is observed with a mid-peak potential of 2.04 V, while

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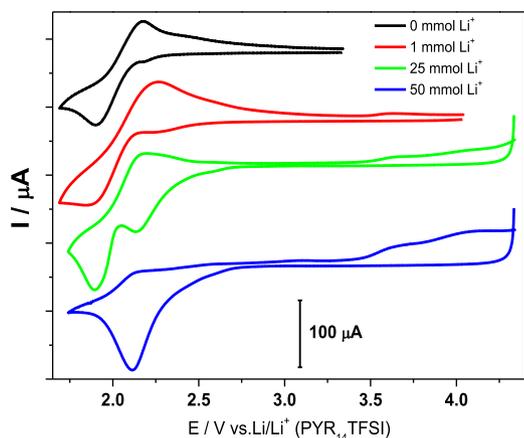[z]E-mail: calvo@qi.fcen.uba.ar

**Figure 1.** Cyclic voltammetry experiment of $O_2$ saturated $PYR_{14}TFSI$ + LiTFSI at different $Li^+$ concentrations 0–50 mM at 50 mV.s$^{-1}$.

a cathodic ORR peak at 1.91 V is in good agreement with previous reports.[14,15] In the reverse scan an oxidation peak at 2.16 V corresponds to the oxidation of superoxide at the electrode surface which has not diffused away from the electrode surface, i.e. the reaction $O_2/$ $PYR_{14}^+O_2^-$ is reversible.

As we introduce 1 to 25 mM LiTFSI in the ionic liquid the quasi reversible peak is still observed but a second oxygen reduction peak at more positive potential, ie. 2.15 V is now present due to the formation of $Li^+O_2^-$ ion pair. The $O_2/LiO_2$ redox couple exhibits a more positive potential than $O_2/$ $PYR_{14}^+O_2^-$ due to the effect of a better acceptor cation.[20]

At 50 mM LiTFSI a single cathodic peak at 2.15 V is observed and the superoxide re-oxidation peak disappears, while anodic current is observed above 3.4 V from 25 mM lithium ion concentration. Thus, the $O_2/$ $PYR_{14}^+O_2^-$ reaction does not contribute to the current at high $Li^+$ concentration. Under stirring with a rotating disc electrode system convective-diffusion ORR plateau is observed in Figure 2 for the lithium free $PYR_{14}TFSI$ and cathodic peaks are present in lithium containing electrolyte.
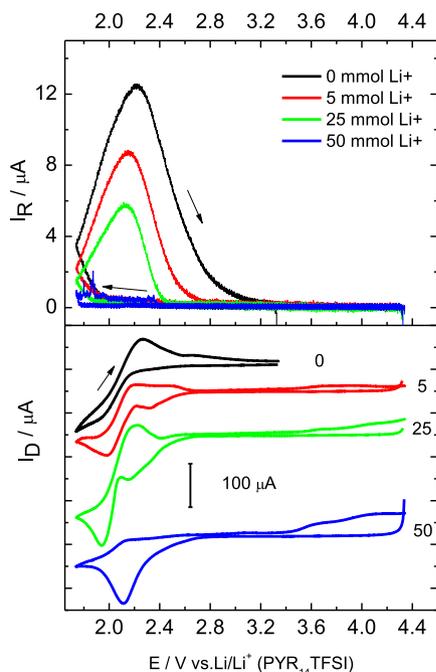
An RRDE study of the ORR in $PYR_{14}TFSI$ containing LiTFSI shows that superoxide ion can be detected at the ring electrode, see Figure 2. However the ring electrode response is delayed in time (potential in the cyclic voltammetry) with respect to the ORR onset at the disc electrode. Similar findings have been reported for $O_2$ saturated pure $Pyr_{14}TFSI$ and have been ascribed to the slow diffusion of $O_2^-$ radical anion in the ionic liquid.[17] While the diffusion coefficient for neutral $O_2$ in $PYR_{14}TFSI$ is $2.9 \times 10^{-6}$ cm$^2$.s$^{-1}$,[15] superoxide exhibits a negative charge and therefore the diffusion coefficient in the highly charged ionic liquid is much lower, i.e. $1.1 \times 10^{-7}$ cm$^2$.s$^{-1}$.[17]

The slow diffusion of superoxide is also responsible for the positive currents in the back scan due to the oxidation of superoxide radical that has not completely diffused away from the disc electrode surface at positive enough potentials for its anodic oxidation.

Figure 2 features the strong effect of lithium ion concentration: The yield of superoxide ion detected at the ring electrode decreases and the disc current pre-peak at 2.15 V increases the higher the LiTFSI concentration. Therefore, insoluble $Li_2O_2$ becomes the main interfacial electrode reaction product at 50 mM LiTFSI with no detection of superoxide at the ring electrode.

Notice that the solubility of oxygen in $PYR_{14}TFSI$ is 13.6 mM,[6] and therefore the $O_2^-$ concentration is much less than the ionic liquid cation $PYR_{14}^+$ concentration, thus $PYR_{14}^+$ $O_2^-$ prevails, but above 25 mM $Li^+$, surface $Li^+O_2^-$ is more favorably formed due to the strong Lewis acidity of small $Li^+$ cations and the shortly lived $Li^+O_2^-$ disproportionates into $Li_2O_2$ and oxygen.

Superoxide is the first oxygen reduction product as shown by Frith et al.[21] who have reported a Raman band at 1107 cm$^{-1}$ assigned to superoxide anions during the ORR in $O_2$ saturated $PYR_{14}TFSI$ containing 10 mM LiTFSI. At low concentration of hard Lewis acid $Li^+$ cations and high concentration of soft organic cations $PYR_{14}^+$ these can associate to the superoxide ion, and therefore, prevent them from combining to form $Li_2O_2$. As the LiTFSI concentration increases, the main surface reaction product is $Li_2O_2$ as has been shown in this electrolyte by ex-situ the 805 cm$^{-1}$ Raman spectroscopy band characteristic of lithium peroxide[22] and confirmed in the present study by the EQCM mass increase in Figure 3. In spite of the noisy data due to the high viscosity of the ionic liquid, there is a clear gravimetric evidence of formation of insoluble $Li_2O_2$ at low overpotentials. Furthermore, notice that the mass increases at the peak due to formation of $Li^+O_2^-$, which we take as an evidence of disproportionation.

DEMS for $O_2$ (q/m = 32) and $CO_2$ (q/m = 44) simultaneous to the ORR and re-oxidation in pure $PYR_{14}TFSI$ ionic liquid and in 25 mM LiTFSI in $PYR_{14}TFSI$ under constant current pulses are shown in Figure 4. In both systems $I_{32}$ current decreases due to the $O_2$ depletion during the ORR. After correction for the mass spectrometry ionic current delay (22 seconds) due to transport in the IL and DEMS vacuum, positive $I_{32}$ current for oxygen evolution in pure ionic liquid occurs at about 2 V confirming the anodic peak voltammetry evidence
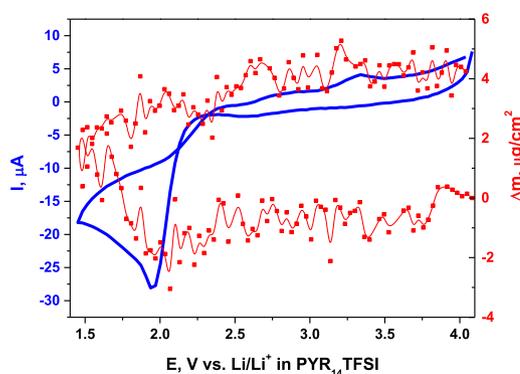


**Figure 2.** Au-Au RRDE experiment of $O_2$ saturated $PYR_{14}TFSI$ + LiTFSI at different $Li^+$ concentrations 0–50 mM, 4 Hz, 50 mV.s$^{-1}$, ring potential 3.0 V, A = 0.2 cm$^2$, $N_o$ = 0.28.



**Figure 3.** Cyclic voltammetry experiment of $O_2$ saturated $PYR_{14}TFSI$ + 0.18 M LiTFSI at 50 mV.s$^{-1}$ and 10 MHz EQCM mass increase ($\Delta$m/A) simultaneous to the cyclic voltammetry.
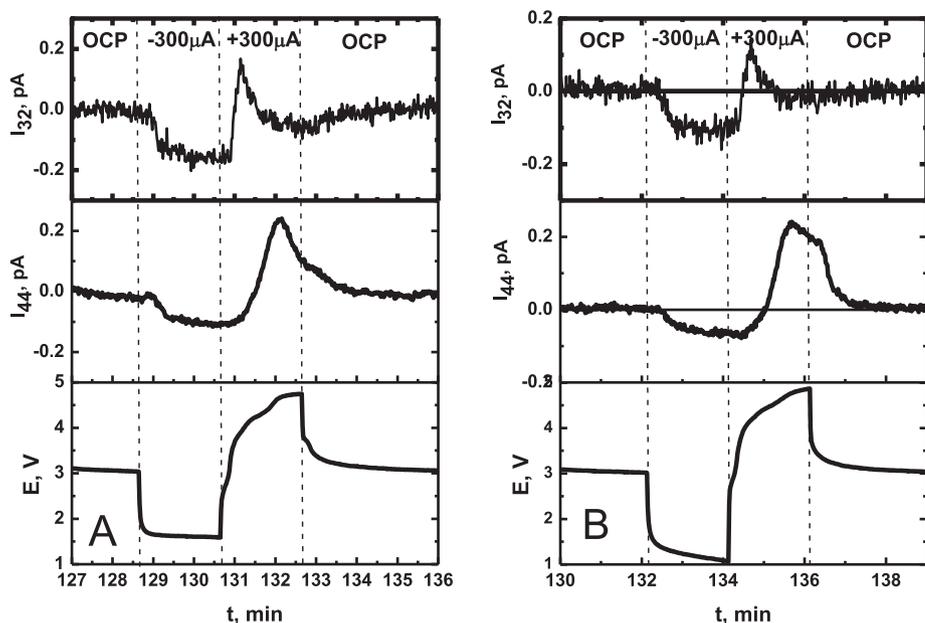
**Figure 4.** DEMS currents for $I_{32}$ and $I_{44}$ respectively and Au electrode potential in $O_2$ saturated $PYR_{14}TFSI$ (A) and $PYR_{14}TFSI + 25$ mM $LiTFSI$ (B) for reduction and oxidation pulses at a $-300$ and $+300\ \mu A$ respectively.

during the back scan and the RRDE detection of superoxide. In 25 mM $Li^+$ solution in $PYR_{14}TFSI$, the mass 32 ionic current peak due to superoxide oxidation is smaller.

It should be noticed that there is no DEMS evidence for $O_2$ evolution expected from $Li_2O_2$ oxidation above 3.2 V while anodic currents are observed in Figures 1 and 2. However, $I_{44}$ mass spectroscopic current due to $CO_2$ increases above 4.2 V consistent with the FTIR evidence of $PRY_{14}^+$ degradation[18] and mass loss in the EQCM experiment. Therefore the parasitic reaction of $Li_2O_2$ with the ionic liquid cation is expected to yield surface species that can only be oxidized at high overpotentials.

## Summary

Competition of ORR product $O_2^-$ for the $PYR_{14}^+$ and the strong Lewis acid $Li^+$ is reflected in the lower yield of soluble superoxide, EQCM mass increase and the positive shift of the $O_2/O_2^-$ potential while increasing the $Li^+$ concentration in the ionic liquid.

## Acknowledgments

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